



What We Claim:

Claims:

A hollow fiber porous membrane made of a perfluorinated thermoplastic polymer having an essentially skinless surface on at least one surface and an IPA flow time of less than about 3000 seconds.

- 2. The membrane of Claim 1 wherein said membrane is asymmetric.
- 10 3. The membrane of claim 1 or 2 wherein the IPA flow time is less than about 2000 seconds.
 - 4. The membrane of Claim 1 or 2 wherein the IPA flow time is less than about 1500 seconds
 - 5. The membrane of claim 1 or 2 wherein said perfluorinated thermoplastic polymer is poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) or poly(tetrafluoroethylene-co-hexafluoropropylene).
- 20 6. The membrane of Claim 5, wherein the alkyl of said poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) is propyl, methyl, or blends of methyl and propyl.
- 7. A method of producing a hollow fiber porous membrane from a perfluorinated thermoplastic polymer having an essentially skinless surface on at least one surface comprising;
 - a) dissolving said perfluorinated thermoplastic polymer in a solvent that forms an upper critical solution temperature solution with said polymer,
- b) extruding said solution through an annular die, a portion of said die being submerged in a cooling bath, and maintained at a temperature sufficiently high to prevent said solution from prematurely cooling,
 - c) extruding said solution into said cooling bath,

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- d) cooling said solution to below the upper critical solution temperature to cause separation into two phases by liquid-liquid phase separation, said phases being a polymer rich solid phase, and a solvent rich liquid phase, to form a gel fiber,
- e) extracting said solvent from said gel fiber to form a porous hollow fiber membrane,
 - f) drying said porous hollow fiber membrane under restraint.
- 8. The method of Claim 7 wherein said portion of said die being submerged is the die tip.
 - 9. The method of Claim 7 wherein said perfluorinated thermoplastic polymer is dissolved in a concentration of from about 12% to about 35% by weight in a solvent that forms an upper critical solution temperature solution with said polymer.
 - 10. The method of Claim 7 wherein step (b) comprises extruding said solution in an essentially horizontal attitude through an annular die, said die maintained at a temperature sufficiently high to prevent said solution from prematurely cooling, wherein the tip of said die penetrates through a wall separating said the body of said die from cooling bath, exposing the die exit to said cooling bath/liquid.
- 11. The method of Claim 7 wherein the solvent has a boiling point lower than the temperature of the gel fiber at the die tip exit.
 - 12. The method of Claim 7 wherein the solvent is a low molecular weight saturated chlorotrifluorohydrocarbon polymer.
- 30 13. The method of Claim 12 wherein the solvent is HaloVac® 60 or HaloVac® 56 or blends thereof.



14. The method of Claims 7, 8, 9, 10, 11, 12, or 13 wherein said perfluorinated thermoplastic polymer is poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) or poly(tetrafluoroethylene-co-hexafluoropropylene).

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- 15. The method of Claim 14 wherein the alkyl of said poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) is propyl, methyl, or of blends of methyl and propyl.
- 10 16. The method of Claims 7, 8, 9, 10, 11, 12, or 13 wherein said cooling bath liquid consists of a non-solvent for said perfluorinated thermoplastic polymer.
 - 17. The method of Claim 14, wherein said cooling bath liquid consists of a non-solvent for said perfluorinated thermoplastic polymer.
 - 18. The method of Claims 7, 8, 9, 10, 11,12, or 13 wherein said cooling bath liquid consists of the group selected from silicone oil or dioctylpthalate.
- 20 19. The method of Claim 14, wherein said cooling bath liquid consists of the group selected from silicone oil or dioctylpthalate.
- 20. A hollow fiber porous membrane produced from a perfluorinated thermoplastic polymer having an essentially skinless surface on at least one surface, and a IPA flow time of less than about 3000 seconds produced by the method of Claims 7, 8, 9, 10, 11, 12, or 13.
 - 21. The membrane of Claim 20 wherein said membrane is asymmetric.
- 30 22. The membrane of Claims 20 wherein said perfluorinated thermoplastic polymer is selected from the group consisting of poly(tetrafluoroethylene-coperfluoro(alkylvinylether)) or poly(tetrafluoroethylene-cohexafluoropropylene).

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- 23. The membrane of Claim 22, wherein the alkyl of said poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) is selected from the group consisting of essentially all propyl, of essentially all methyl, or blends of methyl and propyl.
- 24. The membrane of Claim 21 wherein said perfluorinated thermoplastic polymer is selected from the group consisting of poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) or poly(tetrafluoroethylene-co-hexafluoropropylene).
- 25. The membrane of Claim 24, wherein the alkyl of said poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) is selected from the group consisting of essentially all propyl, of essentially all methyl, or blends of methyl and propyl.
- 26. A hollow fiber contractor membrane made of a perfluorinated thermoplastic comprising a porous surface on both diameters.
- 27. A hollow fiber contactor membrane made of perfluorinated thermoplastic comprising a unskinned surface both diameters capable of liquid-gas mass transfer with a Sherwood number equal to about 1.64 times the Graetz number to the 0.33 power in a range of Graetz numbers of from about 5 to about 1000.
- 28. The membrane of any one of Claims 26 and 27 wherein said perfluorinated thermoplastic polymer is selected from the group consisting of poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) and poly(tetrafluoroethylene-co-hexafluoropropylene).
- 29. The membrane of Claim 28 wherein the alkyl of said poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) is selected from the group consisting of propyl, methyl, and blends of methyl and propyl.